



Valorisation of glycerol by condensation with acetone over silica-included heteropolyacids

P. Ferreira^a, I.M. Fonseca^b, A.M. Ramos^b, J. Vital^b, J.E. Castanheiro^{a,*}

^a Centro de Química de Évora, Departamento de Química, Universidade de Évora, Rua Romão Ramalho, No. 59, 7000-671 Évora, Portugal

^b REQUIMTE, CQFB, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

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ABSTRACT

The acetalisation of glycerol was studied using heteropolyacids, immobilized in silica, as catalysts, at 70 °C. The main product of glycerol acetalisation was solketal. The tungstophosphoric (PW), molybdophosphoric (PMo), tungstosilicic (SiW) and molybdosilicic (SiMo) acids were immobilized in silica by sol–gel method.

It was observed that the catalytic activity decreases in the series: PW.S > SiW.S > PMo.S > SiMo.S. All catalysts exhibited good values of selectivity to solketal (about 98% near complete conversion). The effect of different parameters, such as catalyst loading, molar ratio of glycerol to acetone and temperature on the glycerol acetalisation, over PW.S catalyst, was studied. Catalytic stability of the PW.S, SiW.S, PMo.S and SiMo.S catalysts was evaluated by performing consecutive batch runs with the same catalyst sample. After the third batch, it was observed a stabilisation of the initial activity.

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1. Introduction

Glycerol is the by-product of biodiesel production by transesterification of triglyceride with methanol or ethanol. In the last years, an increase of biodiesel production has been observed. For every 9 kg of biodiesel produced, about 1 kg of a crude glycerol is formed. By consequence, an increase of glycerol production and a price decrease turns glycerol a promising low-cost feedstock for producing value-added chemicals or materials. A lot of work has been devoted to the transformation of glycerol by various catalytic processes involving reforming, oxidation, hydrogenolysis etherification and esterification [1–7].

The condensation of glycerol with acetone can become a possible solution to the problem, which provides a branched oxygen-containing compound. These compounds could be used as additives in the biodiesel formulation, improving the cold properties and lowering the viscosity [8]. The products of glycerol acetalisation are (2,2-dimethyl-[1,3]dioxan-4-yl)-methanol (solketal) (A) and 2,2-dimethyl-[1,3]dioxan-5-ol (B) (Scheme 1).

Traditionally, the condensation of glycerol with acetone is carried out over mineral acids as catalysts. However, the effluent disposal leads to environmental problems and economical inconveniences. These problems can be overcome by the use of heterogeneous catalysts. Only a few works have been found

dealing with solid catalysts, including zeolites and Amberlyst [9,10].

Heteropolyacids (HPAs) with the Keggin structure are known to be highly active heterogeneous catalysts in acid type reactions. However, the HPAs have some disadvantages as catalysts, such as their low thermal stability, low surface area (1–10 m²/g), separation problem from reaction mixtures and solubility [11,12]. In order to overcome these disadvantages, a great variety of supports, such as zeolites [13–16], activated carbons [17–19], silica [20–23] and polymers [24–27], have been used as support to immobilize HPAs. Heteropolyacids included in silica have attracted interest as a non-leaching solid acid catalyst, suitable for reactions in polar media [28].

Heteropolyacids have been used as acid catalysts in reactions involving glycerol, such as dehydration [29–32], esterification [15,33] and dichloropropanol synthesis [34].

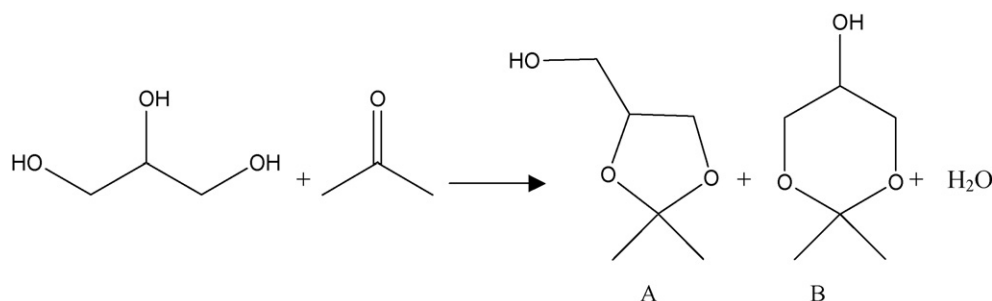
In this work, we report the acetalisation of glycerol over silica-included heteropolyacids. The influence of various reaction parameters, such as temperature, molar ratio of glycerol to acetone and catalyst loading, on the activity of the most active catalyst, is also studied.

2. Experimental

2.1. Catalysts preparation

The catalysts samples were prepared according to Izumi et al. [35], by sol–gel technique. A mixture of water (2.0 mol), 1–

* Corresponding author. Tel.: +351 266745311; fax: +351 266744971.
E-mail address: jefc@uevora.pt (J.E. Castanheiro).



Scheme 1.

butanol (0.2 mol) and heteropolyacid (5.0×10^{-4} mol) was added to tetraethyl orthosilicate (0.2 mol) and stirred at 80°C during 3 h. After this period, the hydrogel obtained was dehydrated slowly at 80°C for 1.5 h, in vacuo (25 Torr). The dried gel obtained was extracted in soxhlet apparatus with methanol during 72 h and dried at 100°C overnight.

Samples will be denoted by the PW.S, SiW.P, PMo.S and SiMo.S for the catalyst prepared from tungstophosphoric acid (PW), tungstosilicic acid (SiW) molybdophosphoric acid (PMo) and molybdosilicic acid (SiMo) immobilized in silica, respectively.

2.2. Catalysts characterization

Textural characterization was based on the nitrogen adsorption isotherm, determined at 77 K with a Micromeritics ASAP 2010 apparatus.

The amount of Mo and W in silica catalysts was measured by dissolving the catalyst in $\text{H}_2\text{SO}_4/\text{HF}$ 1:1 (v/v) and analysing the obtained solution by inductively coupled plasma analysis (ICP), which was carried out in a Jobin–Yvon ULTIMA instrument.

FTIR spectroscopy in KBr pellets was carried out on a Bio-Rad FTS 155 spectrometer. The spectra were taken with a resolution of 4 cm^{-1} in the range of $400\text{--}4000\text{ cm}^{-1}$, by running 1000 scans.

The X-ray diffraction (XRD) patterns of the heteropolyacid, silica and catalysts were obtained by using a Bruker powder diffractometer with built-in recorder, using $\text{Cu K}\alpha$ radiation, nickel filter, 30 mA and 40 kV in the high voltage source, with a scanning angle between 10° and 60° of 2θ at a scanning rate of $1^\circ/\text{min}$.

Catalyst acidity was measured by means of potentiometric titration, according to Pizzio et al. [36]. A small quantity of *n*-butylamine solution (0.05 N) in acetonitrile was added to a known mass (0.05 g) of solid suspended in acetonitrile (90 mL), and shaken for 3 h. The suspension was then potentiometrically titrated with the same solution of *n*-butylamine in acetonitrile. The electrode potential variation was measured with a Crison microPH 2001 instrument.

2.3. Catalytic experiments

The catalytic experiments were carried out in a stirred batch reactor at 70°C . In a typical experiment, the reactor was loaded with 30 cm^3 of acetone and 4 g of glycerol. Reactions were started by adding 0.2 g of catalyst.

Stability tests of the catalysts (PW.S, SiW.S, PMo.S and SiMo.S) were carried out by running four consecutive experiments, under the same reaction conditions. Between the catalytic experiments, the catalyst was separated from the reaction mixture by filtration, washed with acetone and dried at 110°C overnight.

A blank experiment was carried out, in the absence of catalyst, being kept all the other conditions.

Samples were taken periodically and analysed by GC, using a KONIC HRGC-3000C instrument equipped with a $30\text{ mm} \times 0.25\text{ mm}$ DB-1 column.

3. Results and discussion

3.1. Characterization of catalyst

The nitrogen adsorption–desorption isotherms of the catalysts are Type I, according to the IUPAC classification, which is characteristic of a microporous material. The textural characterization (BET specific area (S_{BET}), microporous volume (V_{micro}) and total porous volume) is shown in Table 1. It can be observed that the microporous volume is similar to the total porous volume of the materials, indicating that the catalysts are microporous materials. In fact, the immobilization of the heteropolyacids in silica, by sol–gel method, creates a microporous material and the heteropolyacids are incorporated in the silica pores, during the catalyst synthesis [35]. In Table 1, it can also be observed a decrease in the total porous volume of silica with an increase in the heteropolyacid amount.

Pore size distributions were calculated using the desorption branch of the nitrogen adsorption–desorption isotherms and the BJH method. Fig. 1 shows the pore size distribution of silica-included heteropolyacids. The catalysts are porous materials with

Table 1
Physicochemical characterization of silica-included heteropolyacids.

Sample	HPA load ^a (wt%)	Surface area ^b (m^2/g)	Microporous volume ^c (cm^3/g)	Total porous volume ^d (cm^3/g)	Keggin-anion density ^e /HPA nm^{-2}
Silica	–	223	0.02	0.46	–
PW.S	4.2	458	0.24	0.25	0.019
SiW.S	5.7	332	0.16	0.16	0.036
PMo.S	3.7	478	0.25	0.26	0.026
SiMo.S	3.9	466	0.24	0.25	0.028

^a HPA load determined by ICP analysis.

^b BET.

^c *t* Method.

^d (p/p°)=0.98.

^e Keggin-anion density (HPA nm^{-2}) = $\frac{[\text{HPA loading (wt\%)} / 100] \times 6.02 \times 10^5}{\text{BET surface area of catalyst (m}^2 \text{ g}^{-1}) \times \text{MM (HPA)}}$.

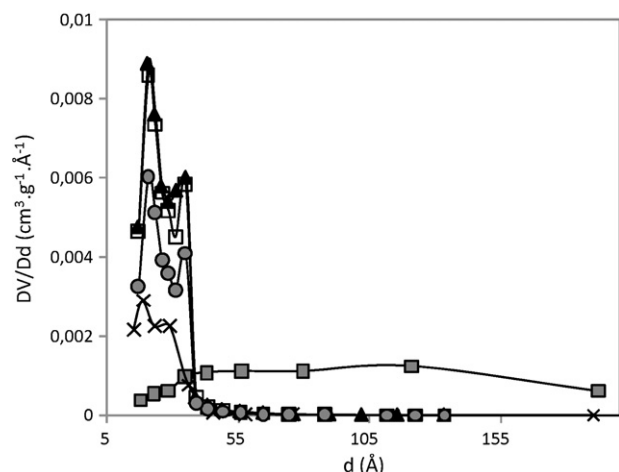


Fig. 1. Pore size distribution of silica-included heteropolyacids. (■) Silica, (▲) PW.S, (□) SiW.S, (●) PMo.S and (×) SiMo.S.

micropores and mesopores. Similar result was also observed by Izumi et al. [37].

The Keggin-anion density of the catalysts (HPA nm⁻²), expressed as the number of Keggin anions per square nanometre, was calculated according to the actual HPA loading and catalyst surface area (Table 1). The surface coverage of catalyst was calculated according to a literature method using the following equation [30]:

$$\text{Keggin-anion density (HPA nm}^{-2}\text{)} = \frac{[\text{HPA loading (wt\%)/100}] \times 6.02 \times 10^5}{\text{BET surface area of catalyst (m}^2 \text{ g}^{-1}\text{)} \times \text{MM (HPA)}}$$

where MM(HPA) is the molecular weight of the heteropolyacids.

It was observed that all catalysts showed low Keggin-anion density, and when the heteropolyacid amount immobilized in silica increases, the density increases as well. Similar results were also observed by Atia et al. [29] and Chai et al. [30].

FTIR spectra of the heteropolyacids supported in silica are shown in Fig. 2. There are four different kinds of oxygen atoms, in Keggin-anion structure [XM₁₂O₄₀]ⁿ⁻, according to the location they take in that unit: oxygen atoms bound to three M atoms and to the X heteroatom (O_a), bridging oxygen atoms (O_b and O_c), and terminal oxygen atoms (O_d). The symmetric and asymmetric vibrations of different M–O bonds are observed in the following regions of the vibration spectra: M–O_d bonds (1000–960 cm⁻¹), M–O_b–M bonds

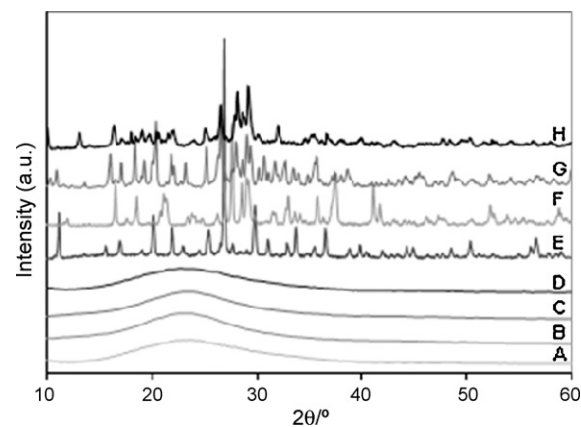


Fig. 3. XRD patterns of (A) SiW.S, (B) SiMo.S, (C) PMo.S, (D) PW.S, (E) PMo, (F) SiW, (G) PW and (H) SiMo.

(890–850 cm⁻¹), and M–O_c–M bonds (800–760 cm⁻¹) [38]. However, some bands, typical of HPA Keggin structures, are overlapped or partially overlapped with the bands of the silica matrix framework.

Fig. 3 shows the XRD patterns of the pure heteropolyacids and silica-included heteropolyacids. It is observed that a broad band centered around 2θ = 25°, which is associated to the amorphous silica. No crystalline phases related to heteropolyacid are observed. This result indicates that the particles are too small or well dispersed to be detected by XRD. Kozhevnikov has found that at higher loadings, 30–50% of HPA is present as a crystalline phase on silica, with 200–300 m²/g, but at lower loadings, mainly fine dispersed species are formed. XRD detectable HPA crystal phase is developed on silica surface only above 20% loading [11]. Molnár et al. [39] also observed similar results. The low value of surface density (Table 1) indicates higher dispersion of HPA over the silica, which could explain why XRD of the catalysts did not show any crystalline phases related to the heteropolyacid. Atia et al. [29] also observed similar behaviour.

The potentiometric titration curves, with *n*-butylamine, obtained for the silica and the catalysts are presented in Fig. 4. The initial electrode potential (*E*_i) indicates the maximum acid strength of the surface sites [36]. The acidic strength of surface sites can be assigned according to the following ranges: very strong site, *E*_i > 100 mV; strong site, 0 < *E*_i < 100 mV; weak site, –100 < *E*_i < 0 mV and very weak site, *E*_i < –100 mV [36]. Table 2

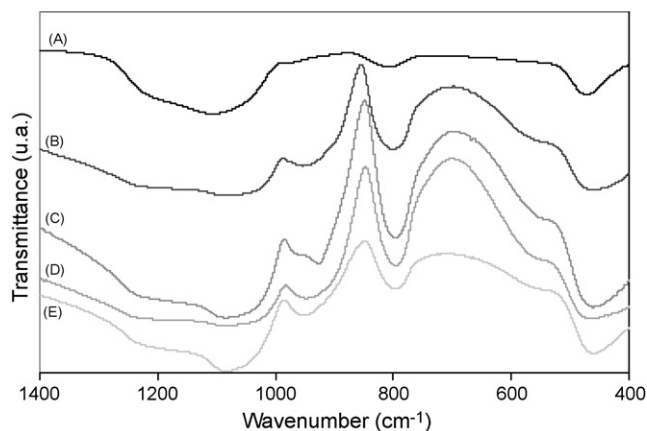


Fig. 2. FTIR spectra of catalysts: (A) silica, (B) PMo.S, (C) SiW.S, (D) SiMo.S and (E) PW.S.

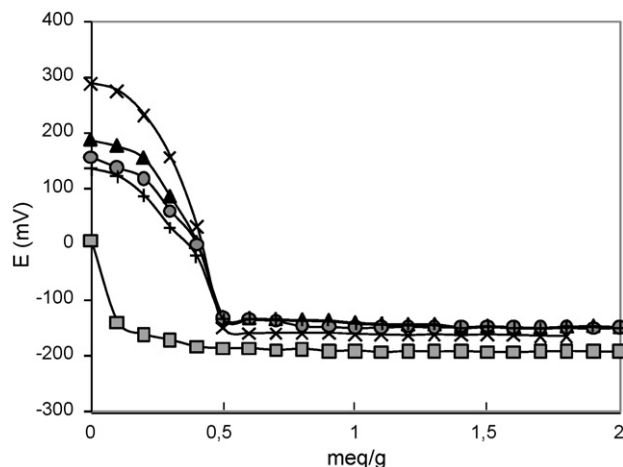


Fig. 4. Potentiometric titration of the catalysts. (■) Silica, (+) SiMo.S, (▲) SiW.S, (×) PW.S and (●) PMo.S.

Table 2
Initial electrode potential (mV) of the catalysts.

Sample	E_i (mV)
Silica	8
PW.S	290
SiW.S	189
PMo.S	158
SiMo.S	137

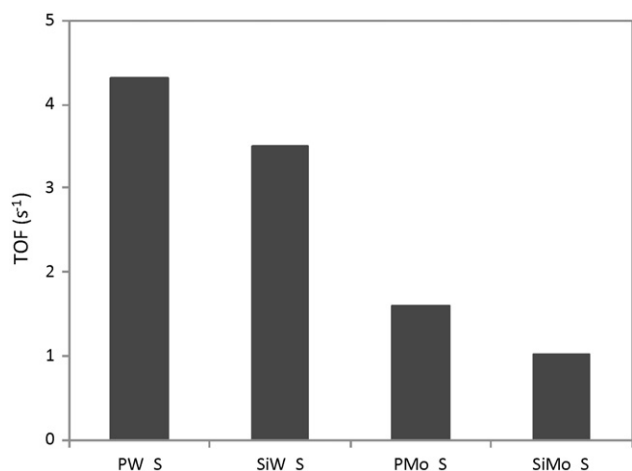


Fig. 5. Acetalisation of glycerol over heteropolyacids immobilized in silica. Initial activities (TOF) taken as the maximum observed reaction rate, calculated from the maximum slope of the glycerol kinetic curve. Reaction conditions: molar ratio of glycerol to acetone = 1:6; temperature = 70 °C; catalyst loading = 0.2 g.

shows the maximum strength of the catalysts. It is observed that the PW.S sample shows the highest maximum strength.

3.2. Catalytic experiments

The main product of the glycerol condensation with acetone over heteropolyacids immobilized in silica was solketal (A) being 2,2-dimethyl-[1,3]dioxan-5-ol (B) also formed (Scheme 1).

Fig. 5 shows the initial activity, expressed in Turnover Frequency (TOF (s^{-1})), of silica-included heteropolyacids (PW.S, SiW.S, PMo.S and SiMo.S) in the glycerol acetalisation. It was observed that the catalytic activity increases in the following order: SiMo.S < PMo.S < SiW.S < PW.S. This behaviour can be explained due to the increase of the catalysts acid strength (Table 2).

All catalysts used in the glycerol acetalisation exhibited high selectivity towards solketal (about 97% at a near glycerol complete conversion). A possible explanation is shown in Scheme 2. The glycerol acetalisation leads to formation of the hemiketal. The dehydration yields a tertiary carbenium ion, which can be stabilized by resonance with the non-bonded electron pairs of the adjacent oxygen atom. Then, a quick nucleophilic attack of the secondary hydroxyl group occurs to form the five-member ring ketal. As the lifetime of the carbenium ion in the reaction medium is supposed to be short, compared with the lifetime of the hemiketal, the product

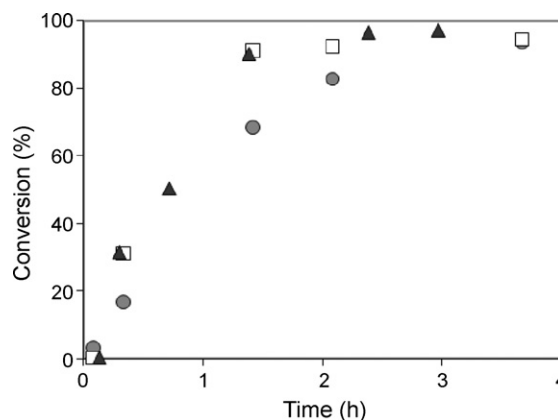


Fig. 6. Acetalisation of glycerol over PW.S catalyst. Effect of the reaction temperature. Conversion (%) versus time (h): (●) $T = 40$ °C; (□) $T = 55$ °C; (▲) $T = 70$ °C. Reaction conditions: molar ratio of glycerol to acetone = 1:6; catalyst loading = 0.2 g.

distribution is governed by kinetics, which favours the formation of the less thermodynamically stable five-membered ring transition state, as already observed in other cyclisation reactions [9,40].

In order to optimise the reaction conditions, the effect of different parameters (catalyst loading, molar ratio of glycerol to acetone and temperature) on glycerol acetalisation over PW.S catalyst was studied.

3.3. Influence of reaction parameters

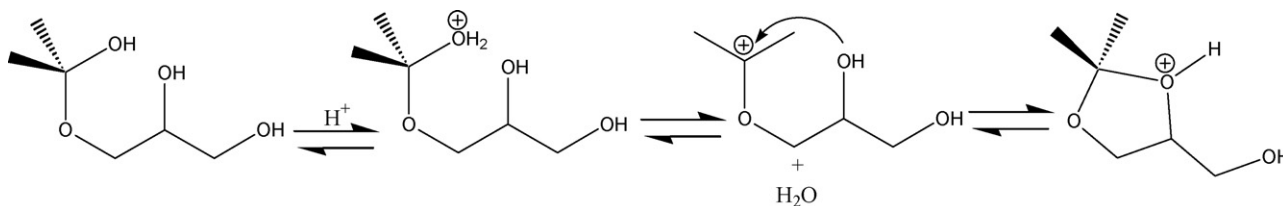
3.3.1. Reaction temperature

In order to evaluate the influence of reaction temperature on glycerol condensation with acetone over PW2.S, different experiments were carried out. The reaction temperature varied from 40 °C to 70 °C, while the molar ratio glycerol:acetone and the amount of catalysts were kept constant. Fig. 6 shows the glycerol conversion versus time (h). It was observed that the glycerol conversion slightly increases with temperature. In the cyclohexanone acetalisation with methanol over Al-MCM-41, as catalyst, Rabindran Jermy et al. [41] observed that when the reaction temperature increases from 100 °C to 120 °C, the cyclohexanone conversion increases from 86.8% to 87.8%, after 8 h.

At the different temperatures studied, similar values of selectivity to solketal (about 97–99% at near complete conversion) were obtained.

3.3.2. Catalyst loading

In order to study the effect of catalyst loading on the glycerol conversion, different loadings of PW.S were used in the condensation of glycerol with acetone. The temperature and the molar ratio of glycerol:acetone were kept constant. Fig. 7 shows the effect of catalyst loading (PW.S) on the glycerol conversion. It was observed that the glycerol conversion increases when the catalyst loading increases from $m = 0.1$ g to $m = 0.2$ g. The time required to reach the reaction equilibrium was reduced. These results can be explained due to the increase of total number of acid sites available. Similar



Scheme 2.

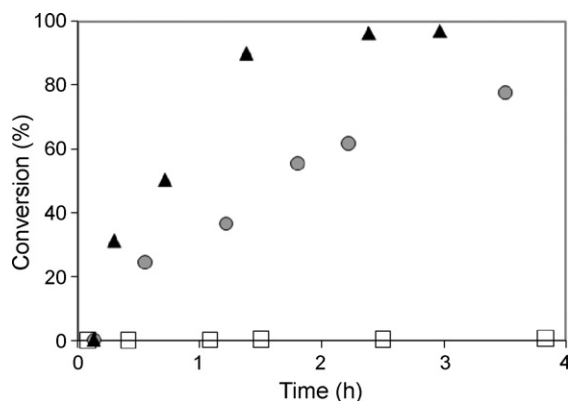


Fig. 7. Acetalisation of glycerol over PW.S catalyst. Effect of the catalyst loading. Conversion (%) versus time (h): (□) without catalyst; (●) $m = 0.1$ g; (▲) $m = 0.2$ g. Reaction conditions: molar ratio of glycerol to acetone = 1:6; temperature = 70 °C.

results were also observed by Rabindran Jermy et al. [42] in condensation of benzaldehyde with pentaerythritol over heteropolyacids supported on MCM-41. When the acetalisation of glycerol was carried out in the absence of catalyst, no glycerol conversion was observed (Fig. 7).

The selectivity of PW.S catalyst to solketal was not changed with the increase of catalyst loading (about 97% at near complete conversion).

3.3.3. Molar ratio of glycerol to acetone

The influence of molar ratio of glycerol to acetone on the glycerol conversion was also studied. The catalytic experiments were carried out at reaction temperature of 70 °C, for sample PW.S, while the glycerol/acetone ratio was varied using the proportions 1:3, 1:6 and 1:12. Fig. 8 shows the effect of the molar ratio glycerol to acetone on the glycerol conversion. An increase in the glycerol with the molar ratio of glycerol to acetone was observed. In the benzaldehyde condensation with pentaerythritol over heteropolyacids supported on MCM-41 [42], similar behaviour was also observed.

The molar ratio of glycerol to acetone did not affect the selectivity to solketal (about 97% at near complete conversion).

3.3.4. Catalysts stability

In order to study the catalytic stability of PW.S, SiW.S, PMo.S and SiMo.S, the catalysts were reused several times. Consecutive batch runs were carried out, with the same catalyst sample and in the same reaction conditions. Fig. 9 shows the initial catalytic activity of the PW.S, SiW.S, PMo.S and SiMo.S catalyst. Only a slight

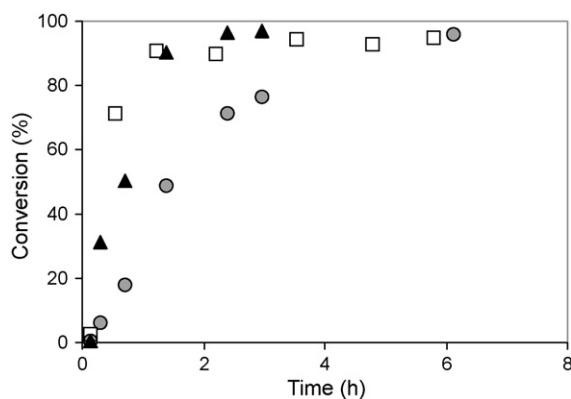


Fig. 8. Acetalisation of glycerol over PW.S catalyst. Effect of the molar ratio of glycerol to acetone. Conversion (%) versus time (h): (●) 1:3; (□) 1:6; (▲) 1:12. Reaction conditions: temperature = 70 °C; catalyst loading = 0.2 g.

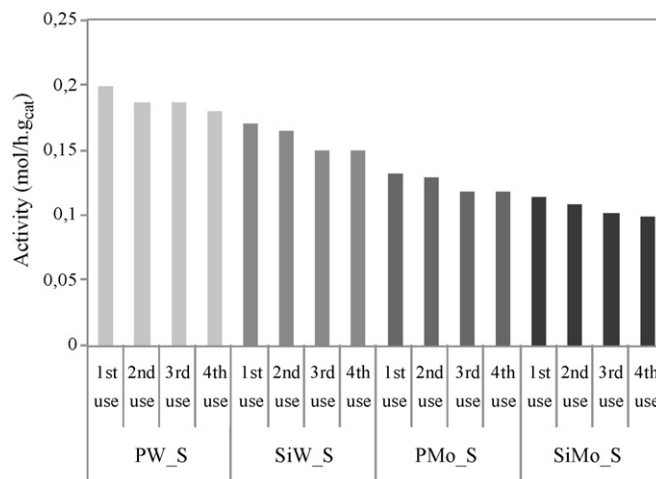


Fig. 9. Stability studies on PW.S, SiW, PMo and SiMo catalysts. Initial activities taken as the maximum observed reaction rate, calculated from the maximum slope of the glycerol kinetic curve.

decrease of the catalytic activity from the first to the fourth run was observed (about 10%, 12%, 11% and 13% for the PW.S, SiW.S, PMo.S and SiMo.S catalyst, respectively).

4. Conclusions

This work demonstrates that HPAs immobilized in silica can be conveniently used as catalysts for the condensation of glycerol with acetone. The preparation method (sol–gel) of heteropolyacids in silica support was an important parameter to the HPAs dispersion and interaction at the support surface. It was observed that the catalytic activity increases in the series: SiMo < PMo.S < SiW.S < PW.S. This behaviour can be explained due to the fact that PW.S is the most acid catalyst of the sequence.

All catalysts tested on acetalisation of glycerol showed high selectivity to solketal (about 97% at near complete conversion).

The catalytic stability was evaluated by performing consecutive batch runs with the same catalyst sample. After the fourth used, the catalysts lost only 10–13% of its initial activity.

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